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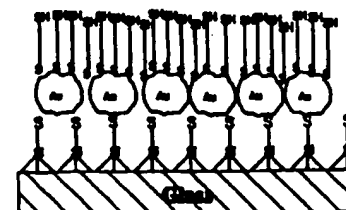
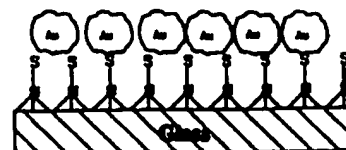
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(54) Title: METHOD OF SYNTHESISING MATERIALS HAVING CONTROLLED ELECTRONIC, MAGNETIC AND/OR OPTICAL PROPERTIES

(57) Abstract

The present invention discloses a method of producing a thin film structure from particles of nanometre dimensions comprising forming at least one layer of metal or semi conductor particles onto a substrate by treating the substrate with a polyfunctional linker molecule so that a first reactive group of the polyfunctional linker molecule reacts with the substrate linking it thereto and subsequently treating the functionalised substrate with a solution of the metal or semi conductor particles so that a second reactive group of the polyfunctional linker molecular reacts with the metal or semi conductor particles linking it thereto.



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DESCRIPTION

METHOD OF SYNTHESISING MATERIALS HAVING CONTROLLED ELECTRONIC, MAGNETIC AND/OR OPTICAL PROPERTIES

The present invention relates to solutions or dispersions containing metal or semi-conductor particles and to a method of synthesising novel materials having controlled electronic, magnetic and/or optical properties therefrom. More particularly it is concerned with solutions or dispersions of small particles, colloids and clusters which particles serve as building blocks in the synthesis of bulk materials and thin film structures with controlled electronic, magnetic and/or optical properties. Such synthesised materials, due to their electronic and optical properties, can then be incorporated into electronic, magnetic and/or optical devices, such as, for example, resistors, diodes, transistors, switches, sensors, displays, lasers photovoltaic and magnetic devices. The method of the invention makes it possible to produce synthesised materials with controlled electronic, magnetic and/or optical properties on the nanometre scale.

A first aspect of the invention concerns the production of the starting materials for the method of the invention. There are two basic starting

materials, a solution or dispersion containing small particles, namely particles having a diameter of from 0.5 nm to 500 nm, and a solution or gas phase of polyfunctional linker molecules. A gas phase can only be utilized if the polyfunctional linker molecule is short and volatile. This is of importance in the production of thin films.

A second aspect of the invention provides methods for linking the small particles in a controlled manner to one another or to other small particles using the same or different linker molecules.

In the case of small metal or semi-conductor particles e.g. colloids, whose typical diameter range is from 10-500 nm, and clusters, whose typical size range is from 0.5 to 10 nm (particles of size 0.5 to 500nm including both colloids and cluster are hereinafter referred to as particles of nanometre dimensions) it was necessary to produce solutions or dispersions which were neither too reactive that the small particles coalesced and precipitated out nor so stable that they could not be reacted.

Solutions or dispersions of metal particles are of course known. However the solutions or dispersions of the art are either too stable that they can not be reacted or are so reactive that the metal particles coalesce and finally precipitate out.

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Typical solutions or dispersions include hydrosols and ligand stabilised colloids or clusters.

In J. Chem Soc Chem Commun, 1994, P. 801, a one step method for the preparation of derivatised nanometre-sized gold particles is described. AuCl_4^- was transferred from aqueous solution to toluene using tetraoctylammonium bromide as a phase transfer reagent and reduced with aqueous sodium borohydride in the presence of a stabilising agent dodecanethiol ($\text{C}_{12}\text{H}_{25}\text{SH}$).

It has now been found that a solution or dispersion containing metal particles of nanodimensions can be produced which is stable yet can be reacted with linker molecules to enable materials to be synthesised in a controlled manner by using an electron solvent donor i.e. a solvent capable of electron donation, for example aromatic compounds or ethers in the presence a phase transfer reagent.

This effect is, without wishing to be bound by theory, believed in part to result from the ability of the solvent to donate electron density to the particles. For example, for aromatic compounds the particles would interact with the π electron system and for ethers with the non bonded electrons.

The term aromatic solvent is used here to include, as well as benzenoid compounds, all compounds

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which display aromaticity such as, for example heterocyclic compounds which can donate π electrons.

According to a first aspect of the present invention there is provided a solution or dispersion consisting essentially of metal particles of nanometre dimensions dissolved or dispersed in an electron donor solvent.

The phase transfer reagent is selected according to the specification of the aqueous metal ion and for an anion is preferably a hydrophobic quaternary ammonium, phosphonium or arsonium ion.

Preferably the electron donor is an aromatic solvent for example toluene, although other solvents capable of donating π electrons such as, for example, benzene, anisole, methylnaphthalene, aniline, xylene and mixtures of the above with polycyclic aromatic compounds such as m-terphenyl, naphthalene and phenanthrene may be used.

The hydrophobic quaternary ammonium, phosphonium or arsonium ions may, for example, be the tetraoctyl ammonium ion $[\text{N}(\text{C}_8\text{H}_{17})_4]^+$. However any straight chained or branched C_3 to C_{16} alkyl or aryl substituted ammonium, phosphonium or arsonium ions could be used, preferably C_5 to C_{10} alkyl substituted quaternary ions.

According to a second aspect of the present

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invention there is provided a method of producing a solution or dispersion of metal particles of nanometre dimensions, the method comprising

- (1) mixing an aqueous solution or dispersion of a metal salt with an electron donor solvent in the presence of a phase transfer reagent for a period sufficient to allow transfer of the metal as metal ions into the organic phase, and
- (2) conducting a reduction step.

The production of stable yet reactive particles of nanometre dimensions allows for the construction of three-dimensional arrays in a controlled manner by way of reacting them with linker molecules. The linker molecules not only determine the potential energy barriers between particle centres but also control the symmetry of the structure of the resultant material. This enables the materials to be synthesised with properties which can be precisely controlled by the chemical nature of the linker molecules. The materials which can be synthesised provide an opportunity to construct unique electronic, magnetic and/or optical devices.

The controlled reaction of the small particles with polyfunctional organic molecules has led to the assembly of three-dimensional structures. The unexpected self-organisation of three-dimensional

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structures allows controlled growth of well-defined materials, the properties of which are dependent on the size and spatial distribution of the particles and on the electronic, magnetic and/or optical properties of the polyfunctional organic molecules. Furthermore, the unexpected simplicity of the method of growth enables the assembly of at least two types of materials:

- i) thin film structures, and
- ii) bulk materials.

The new approach taken is to use polyfunctional linker molecules to link small particles of 0.5 to 500 nm or to attach them to a substrate to yield two-dimensional or three-dimensional structures.

According to a third aspect of the present invention there is provided a two step method of producing a bulk material which comprises

- 1) preparing a solution or dispersion of nanometre sized metal or semi-conductor particles which are neither too stable that they can not be reacted or are so reactive that the particles coalesce and
- 2) reacting said solution or dispersion of said metal or semi-conductor particles with a polyfunctional linker molecule.

In one embodiment this is achieved by firstly preparing a solution or dispersion of metal particles,

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for example gold, in an aromatic solvent, for example toluene, in the presence of hydrophobic quaternary ammonium, phosphonium or arsonium ions, for example a tetraoctylammonium ion and subsequently reacting said solution or dispersion with a polyfunctional linker molecule, for example 1,9 nonanedithiol.

In another embodiment this may be achieved by firstly preparing a solution or dispersion of semiconductor particles and subsequently reacting said solution or dispersion with a polyfunctional linker molecule, for example a silane.

Thus, for example, TiO_2 colloids can be prepared by controlled hydrolysis of titanium alkoxides in the water pools of reverse micellar systems. In the case of indium/tin oxide, a high temperature approach is followed, by the controlled hydrolysis of suitable indium and tin compounds in high temperature solvents, such as, for example m-terphenyl.

Preferably the polyfunctional linker molecule is dissolved or dispersed in the same solvent as the metal or semi conductor particle.

According to a fourth aspect of the present invention there is provided a one step method of producing a bulk material of particles of nanometre dimensions comprising preparing a solution or dispersion of small metal or semi-conductor particles

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in the presence of a polyfunctional linker molecule.

In one embodiment this is achieved by preparing a solution or dispersion of metal particles, for example gold, in an organic electron donor solvent, for example diethyl ether in the presence of a linker molecule, for example 1,9 nonanedithiol.

The linker molecule in this embodiment also acts as a stabilising ligand, preventing coalescence of particles. It is not therefore essential to include hydrophobic quaternary ammonium, phosphonium or arsonium ions.

In another embodiment this may be achieved by preparing a solution or dispersion of a semi-conductor material in the presence of a linker molecule, for example a silane.

According to a fifth and main aspect of the present invention there is provided a method of producing a thin film structure from particles of nanometre dimensions comprising forming at least one layer of metal or semi conductor particles onto a substrate by treating the substrate with a polyfunctional linker molecule so that a first reactive group of the polyfunctional linker molecule reacts with the substrate linking it thereto and subsequently treating the functionalised substrate with a solution of the metal or semi conductor

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particles so that a second reactive group of the polyfunctional linker molecule reacts with the metal or semi conductor particles linking it thereto.

The step of treating the substrate (or an already formed layer of particles) may be by treating it with a solution of linker molecules, so as to react the linker molecules, or by direct reaction such as for example by reacting the linker molecules in the gas phase.

The process can be repeated to build on top of the first layer of metal or semi-conductor particles a plurality of layers of the same or different metal or semi-conductor particles and/or linkers.

Thus, one or more further layers of metal or semi-conductor particles may be formed onto an already formed layer of metal or semi-conductor particles by treating the already formed layer of metal or semi-conductor particles with the same or a different polyfunctional linker molecule so that the same or a different polyfunctional linker molecule reacts with the already formed layer of metal or semi-conductor particles linking the same or different polyfunctional linker molecule thereto to form a functionalised layer of metal or semi-conductor particles and subsequently treating the functionalised layer of metal or semi-conductor particles with a solution of the same or

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different metal or semi-conductor particles to react the second reactive group of the same or different polyfunctional linker molecule with the same or different metal or semi-conductor particles.

Different particles and different linker molecules can be used to produce materials with different properties.

Preferably the polyfunctional linker molecule is dissolved in the same solvent as the metal or semi conductor particles although this is not essential.

Preferably the substrate is treated by first subjecting it to the linker molecule. This is preferably done by immersing it in a solution of the linker molecule although for volatile linker molecules adsorption from the gas phase could be used. Thereafter the functionalised substrate is subjected to the solution or dispersion of the small particles, preferably by immersion. The layer of particles formed on the substrate can then have further layers of small particles formed thereon by repeating the process of adding linkers and further layers of small particles.

The particles can be metal or semi conductor particles so long as they can be generated in solution or dispersion as colloids or clusters.

The preferred particles are the coin metals such

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as, for example, gold, silver and copper, the transition metals, and the elements of groups 1B to IV B of the periodic table. These include aluminium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, germanium, yttrium, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, lanthanum, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, mercury, tellurium and lead.

The metal particles need not be elemental particles and could be alloys. Furthermore, the semiconductor particles include silicon, and arsenides, oxides and chalcogenides or any other materials which show semi-conductor properties and which can be made into particles of nanometre dimensions.

The preferred polyfunctional linker molecules comprise a hydrocarbon skeleton with at least two functional groups (which groups may be the same or different) capable of binding to other particles or a substrate.

They may be electronically neutral or carry a charge.

Examples of the functional groups are

(a) thiols, disulphides, sulphur oxyacids, thiocarbonyl compounds such as thiourea and other

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thioamides and corresponding groups where heavier group VI elements such as selenium and tellurium replace sulphur;

(b) amines, amidines and related groups where heavier group V elements such as phosphorous and arsenic, replace nitrogen, especially phosphines;

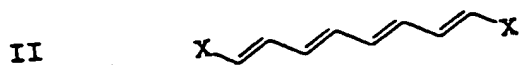
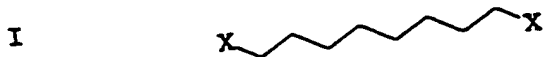
(c) carboxylates and alkynes;

(d) heterocycles : containing nitrogen and/or sulphur as the heteroatom; and

(e) silanes

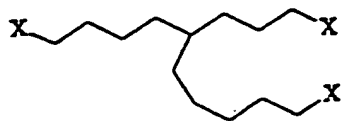
The hydrocarbon skeleton can be a linear or branched aliphatic chain which may contain cyclic moieties, carbon multiple bonds and/or other π -systems. These additional π -systems could be mono- or poly-cyclic aromatic hydrocarbon units including fullerenes (with or without electron donating or electron withdrawing substituents), heterocycles, quinones or metallocene units and embrace chromophoric and ionophoric groups and units capable of acting as redox centres.

Examples of the above include, for example:



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III

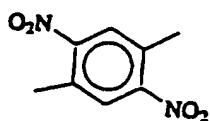


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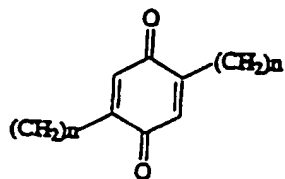


where G is for example;

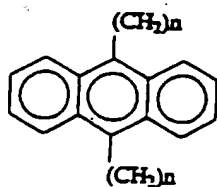
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VI

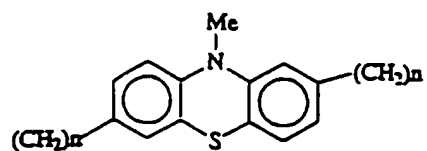


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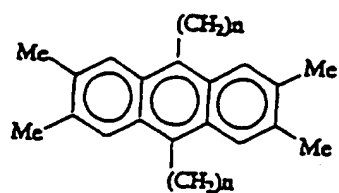


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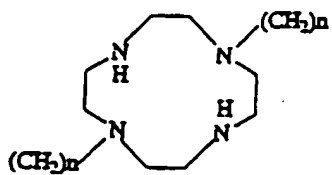
VIII



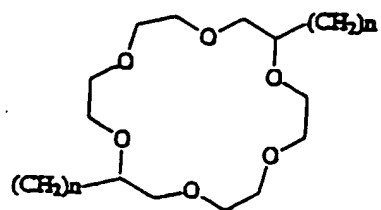
IX



X

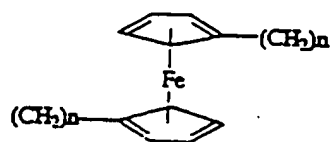


XI



and

XII



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In the above X = a functional group and where more than one X is denoted this may be the same or different

and n = an integer preferably from 0 to 20

The carbon skeletons shown in I, II and III are illustrative of the type of structures and the number of carbon atoms in the chain could vary and is preferably between 2 and 20.

According to a sixth aspect of the invention there is provided a bulk material comprising particles of nanometre dimensions and linker molecules.

According to a seventh aspect of the present invention there is provided a thin film structure comprising a substrate and at least one layer of particles of nanometre dimensions linked thereto by linker molecules.

Preferably there are a plurality of layers of nanosized particles, the particles of each layer being linked by linker molecules.

The particles can be colloids or clusters of metals or semi conductors.

The linker molecule can be any organic molecule with at least two functional groups which groups will react with a substrate and a particle or with two particles:

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Where the particles are metal particles, such as for example, gold or silver or semi conductor particles, such as cadmium sulphide or cadmium telluride, the preferred linkers will be polythiols including dithiols or the corresponding groups where heavier group VI elements such as selenium and tellurium replace sulphur.

Where the particles are semi conductor particle such as, for example, silicon, or a semi conducting metal oxide, the preferred linkers will include silanes as functional groups.

By using polyfunctional linker molecules the resulting material can become part of a growing structure. The growth rate or degree of attachment can be controlled by the type of linker molecule. It is also possible to attach other compounds to the linker molecules.

The electronic, magnetic and/or optical properties of the resulting materials can be preestablished by choosing the appropriate linker molecule and the type and size of the particle.

By using polyfunctional linker molecules having electron donor or acceptor moieties such as, for example, compounds with extended π -systems, quinones, or dinitro or dicyano aromatics, materials displaying n- or p- semi conductor properties can be prepared.

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By using compounds which can act as electron traps, materials can be produced which are electroluminescent.

Furthermore the simplicity of preparation provides a possible route for the preparation of quantum dot, quantum wire and quantum well devices.

According to an eighth aspect of the present invention there is provided a quantum dot, quantum wire or quantum well device comprising a material as hereinbefore described.

The invention will be further described by way of example only, by reference primarily to a system in which the small particles are gold and the linker molecule is a dithiol. Additionally some examples of applications using semi conductor particles as well as metal particles are given.

Example 1

Preparation of colloidal gold particles.

An aqueous solution of hydrogen tetrachloroaurate (30ml, 30 mmol dm^{-3}) was mixed with a solution of tetraoctylammonium bromide in toluene (80ml, 50 mmol dm^{-3}). The two-phase mixture was vigorously stirred until all the tetrachloroaurate was transferred into the organic phase. A freshly prepared aqueous solution of sodium borohydride (25 ml, 0.4 mol dm^{-3})

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was slowly added with vigorous stirring. After further stirring for 3 h the organic phase was separated, washed once with dilute sulphuric acid, twice with sodium carbonate solution, five times with triply distilled water and dried with anhydrous sodium sulphate. Before use, the solution was diluted with toluene to an approximate gold content of 250 mg dm^{-3} based on the assumption that no material was lost during the preparation procedure. The ruby coloured dispersions contain particles, shown by TEM, to be in the range between 6 and 12 nm.

Example 2

Preparation of a solution of linker molecules.

A 2m M solution of 1,9 nonanedithiol was prepared by dissolving the dithiol in toluene.

Example 3

Preparation of bulk materials

Two principally different methods lead to the formation of bulk materials from particles of nanometre dimensions:

(a) precipitation of the material from its solution, and (b) direct synthesis by reduction of the salt in the presence of linker molecules.

Example 3a

Precipitation from solution:

A solution of 1,9 nonanedithiol in toluene as

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described in Example 2 (typically 10 ml, 0.2 mmol dm⁻³) was added to a solution of small gold particles (100 ml, 250 - 500 mg gold dm⁻³, size range 6 - 12 nm) prepared as described in Example 1. The small gold particles precipitate over night quantitatively and form a bulk material as illustrated in Fig 1, which is a schematic representation of the growth of bulk material by self assembly from dissolved metal particles of nanometre dimensions.

Example 3b

Direct synthesis:

A solution of small gold particles was prepared as described in Example 1 but in the presence of 1,9 nonanedithiol in the organic phase. The 1,9 nonanedithiol was added to the reaction mixture immediately before the addition of the reducing agent (sodium borohydride). At least an equimolar amount of 1,9 nonanedithiol with respect to gold is required, but higher ratios are possible. A dark precipitate of the nanomaterial is formed within a few minutes after addition of the reducing agent. The material comprises small gold particles in the size range 1.5 - 3 nm and its resistivity is by at least one order of magnitude higher than that of the comparable material made with small particles in the size range 6 - 12 nm. The activation energy for electron hopping

-20-

is ca. 5 times higher as temperature dependent conductivity measurements on pressed pellets of the material show.

Example 4

Preparation of a thin film structure.

The method for the controlled growth of these materials is the step-wise approach which is shown in Fig. 2 which is a schematic representation of the preparation of a layered structure. More particularly it shows the preparation of nanostructured materials by surface functionalization of the substrate followed by successive attachment of gold nanoparticles and bifunctional linker molecules, in this example, a dithiol, 2A illustrates glass silonization, 2B illustrates attachment of particles, 2C illustrates the formation of a nanometallic structure and 2D illustrates the functionalization of the first layer. This approach gives rise to layered structures comprising monolayers of particles having well-defined two-dimensional conduction properties, separated by linker molecules the electronic properties of which can be controlled by the type of molecule used for the spacer arm between the monolayers. In particular, extended π -systems can be used for accurate control of the electronic properties of the intermediate layers. This method provides a strategy for the design of

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quantum well, quantum wire and quantum dot devices with tailor-made electronic properties as shown in Fig. 3 which is a schematic representation of a multilayer nanostructure array forming quantum dots.

Small particles anchor to a substrate containing linker groups and subsequent growth of layers can then be achieved by alternatively derivatising the surface with for example dithiol and with gold particles. The technique is described by way of an example. Glass microscope slides were functionalised with (3-mercaptopropyl)trimethoxysilane. The functionalised slides were immersed overnight in a solution of colloidal gold in toluene with a gold content of approximately 250 mg dm^{-3} as described in Example 1. The layer of gold particles formed overnight on the glass surface is visible with the naked eye as a slight pink tint. The derivatised slides were washed carefully with toluene and immediately immersed in a 2 mM solution of 1,9-nonanedithiol in toluene prepared as in Example 2. Care was taken that the glass surface was always wetted with toluene to avoid coalescence of surface bound particles. The slides were left in the dithiol solution for 1 h, thoroughly rinsed with toluene and again immersed in the gold dispersion for at least 2 hrs. The formation of the first eight layers was followed by UV/VIS spectroscopy (Fig. 4). The appearance of the material changes from slightly pink (first layer) through purple to deep blue (6th or 7th layer), and develops a golden metallic lustre clearly darker in comparison with a vapour-deposited gold

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film. This colour change might suggest that the particles coalesce to form larger aggregates as already recognised in gold hydrosols by Faraday in 1857. This interpretation was excluded by analysing the material using scanning tunnelling microscopy (STM) (Fig. 5).

Fig. 5 shows a typical STM image of the material obtained with a Burleigh scanning tunnelling microscope. The image shows unambiguously that the individual particles do not coalesce to form bigger units as it is commonly observed for deposits of colloidal metals.

Even after keeping for several weeks in air, no evidence for coalescence was found. If particle growth occurred within the bulk of the material, the electrical conductivity of the film should increase with time and become metallic. No such changes were observed in this case. Temperature dependent resistance measurements were carried out by masking part of the film (38 layer nonanedithiol - Au particles) with a highly conductive silver loaded adhesive and measuring the resistance across a gap of 1 x 2.6 cm as a function of temperature. The result shown in Fig. 6 clearly indicated non-metallic conductivity since the resistance decreases with a rise in temperature. The temperature dependence of the resistivity of this material follows a simple logarithmic law and is shown in Fig. 7. Activated electron hopping is suggested as the principal mechanism of charge transport. An activation energy of $E_a = 0.02$ eV was found, similar to that for

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ultrathin discontinuous metal island films. The resistivity of the material changes dramatically as a function of the chain length of the bifunctional thiols. For example, the resistivity of films made with α , ω -C₆-, C₉- and C₁₂- dithiols increases in the sequence ca. 10, 100, 1000 ohm cm. This observation could not be explained if coalescence of individual particles were a significant feature of the material described here.

It will be apparent from the above example that new materials can be designed by self assembly of small particles using, linking molecules. The electronic properties of such materials are clearly non-metallic and depend on the structure and length of the linker molecule. The size of the individual particles also influences the electronic properties of the material significantly. Those skilled in the art will recognise that these structures constitute quantum dot arrays with properties that are determined by the chemistry of the linker molecules employed.

The preparation described in Fig. 2 is unexpectedly simple. In contrast with semi-conductor physics that require high vacuum deposition methods using complex molecular and atomic beam techniques, the present method involves the use of two solutions, one of nanoparticles and the other of polyfunctional

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linker molecules. The fabrication process comprises simply the successive immersion of the sample on which the device is to be grown in solutions of the above separated by a simple washing step. The operation can be carried out in an open fume cupboard, without the need of sophisticated and high capital cost control equipment.

Nanostructured quantum dot, quantum wire and quantum well materials will be of great importance for the development of the new generation of nanoelectronic devices. The present invention can be regarded as the prototype of a nanostructured array of quantum dots with adjustable electronic conductivity in the range typical for semi conductors. The electronic properties of the material can be tuned by building into the linker molecules, moieties which can act as electron donors or acceptors; n- and p-doping of the material achieved in this way can lead to the fabrication of novel semi conductor devices of nanometre dimensions. The incorporation of compounds with extend π systems of low electronic energy levels leads to the formation of electron traps which could act as light emitting signalling devices. Quantum dot arrays form an ideal basis for the realisation of integrated opto-electronic circuits on the nanometre scale.

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A further application of the invented material is seen in the field of thin film sensors. The dramatic dependence of the electronic conductivity upon structural or electronic changes in the material can be utilised for the detection of, for example, oxidants such as chlorine or ozone.

A further example of the application of the techniques described herein is the preparation of materials, such as, for example, glass modified to benefit from the unique electrochromic effects which can be produced by applying thin film structures to substrates.

The thin film structures can be prepared by functionalising the glass with a mercaptosilane. The functionalisation of surface OH groups with trimethoxypropyl mercaptosilane leads to an -SH terminated surface. By subjecting (for example by dipping) the functionalised surface to a solution as per example 1, a rapid irreversible attachment of clusters to the surface takes place.

The Au-terminated layer can then be derivatised with, for example, a dithiol leading again to an -SE terminated layer. Again, by immersion of the material in the colloidal gold solution, a new layer can be grown. The process can be repeated many times, leading to the growth of multilayers of a material

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formed by clusters joined in a 3-D array by multi-functional organic groups.

The optical and electrical properties of the material are dependent on the organic groups used for joining the metal clusters. For instance, the resistivity is greatly decreased in the order of C₁₆, C₁₂, C₉ and C₆ dithiols. Interestingly, the use of a p-xylene-dithiol results in compounds of very low resistivity, showing the important influence of the potential energy barrier resulting from the presence of the organic linker between the clusters. A schematic model of the type of structures which are probably formed is shown in Fig. 2.

To verify that materials of controlled electrochromic properties can be produced using the methods and solutions of the invention, the potential (and hence, charge) dependence on the optical properties of the thin films produced was characterised. The approach taken consisted in either growing the nanostructured material on transparent ITO electrodes and measuring the modulation of the absorbance of the film by direct transmission, or by reflection, from layers grown on a metallic electrode. These effects were measured by placing the nanostructured material in contact with an unreactive electrolyte solution and measuring the changes in

-27-

reflection when a small potential modulation was applied. To illustrate these effects, an example of the spectral changes induced by potential charges for bulk gold is shown in Fig. 8. This shows the electroreflectance (ER) spectra of bulk Au in 0.1 M KClO_4 , 8 Hz, 150 mV rms, 0.1 V vs saturated calomel electrode (SCE).

For bulk metals, these effects have been successfully analysed in terms of the free electron theory of metals. As can be seen, the effect of applied potentials is small for a bulk metal. This comparatively small change of the spectrum is due to the localisation of the changes in electron distribution caused by the applied potential, to a very narrow surface layer, of 0.05-0.1 nm in thickness. This localisation is a direct consequence of the high electronic concentration, with the resulting very low value of the electric field screening length in the metal.

By contrast, when a few layers of nanosized clusters are chemically attached, a large increase in the ER spectrum is observed, as shown in Fig. 9, which shows the ER spectra for four layers of Au nanoparticles in 0.1 M KClO_4 , 34 Hz, 0.15 V rms. Potentials vs SCE are indicated. The bipolar character of the band observed is due to a true

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electrochromic shift with modulated interfacial field. Thus the results shown in this figure are the difference spectra between nanostructured surfaces at different states of charge. A full description of the physics of this effect cannot be given here.

Two aspects of these important results need highlighting. Firstly, not only the potential modulated absorption increases by nearly a factor of 10 for a nanostructured surface, but most importantly, the position of the ER bands shift with average applied potential. Thus, as the surface of the nanoparticles is made more negative, the absorbance intensity decreases and shifts in wavelength. This can be rationalised in terms of the different contributions to the ER spectrum arising from free and bound electrons with the former becoming dominant as the surface is negatively charged.

The second aspect that is very important from the point of view of the practical applications of these novel materials is the order of magnitude of the effect. From AC impedance measurements it appears that the charge modulation is always localised in the metal layer in contact with the electrolyte solution. Thus, the overall change in reflectance with potential, which is of the order of 0.1%, is localised in a region with a thickness of the diameter of the

-29-

particles used, which was approximately 8 nm in these experiments. Thus, by accessing all the layers of metal clusters for potential modulation, extremely large electrochromic effects, including very large potential dependent absorbance shifts, become possible.

The importance of the effects described is far reaching; it allows for the construction of devices/materials that change reflectance (and the wavelength of absorbance) with applied potentials, for instance, for "smart" window applications.

Yet a further example of the application of the techniques described herein is the preparation of photovoltaic (PV) and infrared (IR) reflecting materials. The applicants having produced a device consisting of nanosized gold particles separated by 1,1'-di(8-thiolo-octyl)ferrocene linkers and mounted on p-si affords a photovoltaic response when irradiated with visible light. Fig. 10 shows the current-potential response of a solid state nanostructured device consisting of:

$n\text{-Si/SiO}_2/\text{mercaptoposilane}/-(\text{Au-D})_4\text{-}/\text{Au}$

$D=1,1'\text{-di(8-thiolo-octyl) ferrocene}$. The response is modulated with chopped illumination and photocurrent generation can be clearly seen. This Fig. illustrates that it is possible to develop a family of self assembled nanostructured tunable photovoltaic materials for applications in a new thin film photovoltaic technology, based on colloidal metal and semiconductor particles using functionalised organic linker

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molecules for attachment and to construct PV cells with the materials developed. The principle of such a device is illustrated in Fig. 11 which is a diagrammatic illustration of the basic structures for the preparation of a solid state TiO_2 sensitised photovoltaic device. VB=valence band; CB= conduction band. The donor and acceptor groups are chemically linked to the TiO_2 nanoparticle and the repeat unit is assembled by the same techniques as described in Fig. 2.

Instead of using metal particles such as, for example, gold, semi conductor particles such as, for example, TiO_2 , indium tin oxide (ITO), and Cds can be used.

Making such a solid state device utilises a sensitiser to inject electrons into the TiO_2 conduction band for sub-band gap excitation wavelengths, and in this approach, charge separation is effected by reaction of the radical cation of the sensitiser with an electron donor. The TiO_2 particles are self-assembled in a structure consisting of linkers incorporating electron transfer donor and acceptor groups, present on opposite sides of the layer of TiO_2 nanoparticles obtained by a step-wise process of the type schematically described with reference to metal particles in Fig. 2.

By suitable manipulation of the electron transfer donor and acceptor groups, the performance can be tuned to the wavelength of the incident radiation.

It is further possible to construct sharp cut-off IR reflectors with, for example ITO by controlling the

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size of the particles forming a film array. IR reflectors are of fundamental importance for ensuring that the temperature of operation of PV modules is kept as low as possible. At present, ITO thin films are prepared by sputtering and the resulting structures are inhomogeneous. The dielectric function of a conductor is dependent, amongst other variables, on doping density and relaxation time of charge carriers. An inhomogeneous material results inevitably in a wide spread of cut-off frequencies and therefore, in a long reflectance tail, as is indeed observed. By preparing, for example, monodisperse ITO by synthesis, followed by derivatisation, fractionation, and fixing of the nanoparticles to glass by chemical means improved devices should result because the methods of the invention will allow uniformity in particle size which in turn leads to sharp IR cut-off characteristics.

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CLAIMS

1. A method of producing a thin film structure from particles of nanometre dimensions comprising forming at least one layer of metal or semi conductor particles onto a substrate by treating the substrate with a polyfunctional linker molecule so that a first reactive group of the polyfunctional linker molecule reacts with the substrate linking it thereto and subsequently treating the functionalised substrate with a solution of the metal or semi conductor particles so that a second reactive group of the polyfunctional linker molecule reacts with the metal or semi conductor particles linking it thereto.

2. A method as claimed in claim 1, wherein the step of treating the substrate with a polyfunctional linker molecule is conducted by treating the substrate with a solution of the linker molecule.

3. A method as claimed in claim 1, wherein the step of treating the substrate with a polyfunctional linker molecule is conducted by treating the substrate with the linker molecule in a gas phase.

4. A method as claimed in any of the preceding claims wherein one or more further layers of metal or semi-conductor particles are formed onto an already formed layer of metal or semi-conductor particles by treating the already formed layer of metal or semi-

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conductor particles with the same or a different polyfunctional linker molecule so that the same or a different first reactive group of the same or different polyfunctional linker molecule reacts with the already formed layer of metal or semi-conductor particles linking the same or different polyfunctional linker molecule thereto to form a functionalised layer of metal or semi-conductor particles and subsequently treating the functionalised layer of metal or semi-conductor particles with a solution of the same or different metal or semi-conductor particles to react the second reactive group of the same or different polyfunctional linker molecules remote with the same or different metal or semi-conductor particles.

5. A method as claimed in claim 4, wherein different linker molecules and/or different metal or semi-conductor particles are used to produce further layers.

6. A method as claimed in claim 4, wherein the same linker molecules and the same metal or semi-conductor particles are used to produce further layers.

7. A method as claimed in any of the preceding claims, wherein the particles of nanometre dimensions are metal particles.

8. A method as claimed in claim 7, wherein the

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metal particles are solutions or dispersion of elemental particles selected from the coin metals, transition metals, elements of groups IB to IVB of the periodic table or alloys and which are neither too reactive that the particles coalesce and precipitate out nor so stable that they can't be reacted

9. A method as claimed in claim 8, wherein the metal particles are present in a solution or dispersion consisting essentially of metal particles of nanometre dimensions dissolved or dispersed in an electron donor solvent.

10. A method as claimed in any of claims 1 to 6, wherein the particles of nanometre dimensions are semi-conductor particles

11. A method as claimed in claim 10, wherein the semi-conductor particles are selected from silicon, oxides and chalcogenides which show semi-conductor properties and which are neither too reactive that the particle coalesce and precipitate out nor so stable that they can't be reacted.

12. A method as claimed in any of the preceding claims, wherein the polyfunctional linker molecules comprise a hydrocarbon skeleton with at least two functional groups which may be the same or different which functional groups are capable of binding to particles or a substrate.

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13. A method as claimed in any of the preceding claims, in which the polyfunctional linker molecule is electrically neutral.

14. A method as claimed in any of claims 1 to 12, in which the polyfunctional linker molecule carries a charge.

15. A method as claimed in claim 12, in which the functional groups of the polyfunctional linker molecule are selected from the group consisting:

(a) thiols, disulphides, sulphur oxyacids, thiocarbonyl compounds and corresponding groups where heavier group VI elements replace sulphur;

(b) amines, amidines and related groups where heavier group V elements, replace nitrogen,

(c) carboxylates and alkynes

(d) heterocycles containing nitrogen and/or sulphur as the heteroatom, and

(e) silanes

16. A method as claimed in claim 15, in which the polyfunctional linker molecule is a dithiol.

17. A method as claimed in any of claims 12 to 16, in which the hydrocarbon skeleton is a linear or branched aliphatic chain which may contain cyclic moieties, carbon multiple bonds and/or other π -systems such as mono or polycyclic aromatic hydrocarbon units including fullerenes, heterocycles,

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quinones or metallocene units.

18. A method as claimed in any of claims 12 to 17, in which the hydrocarbon skeleton is of the type

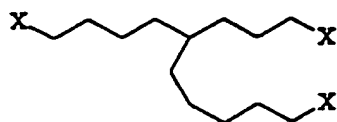
I



II

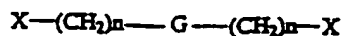


III



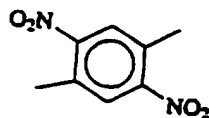
and

IV

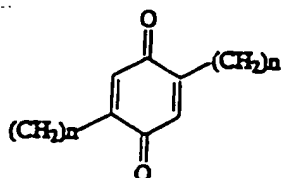


where G is for example;

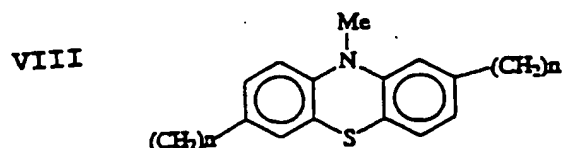
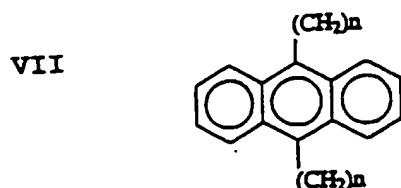
V



VI



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where X is the functional group, n is an integer and in I, II and III the number of carbon atoms in the chain can vary.

19. A method as claimed in any of the preceding claims in which the particles are gold or metal chalcogenides and the linkers are dithiols.

20. A method as claimed in any of claims 1 to 18 in which the particles are silicon, or a semi-conducting metal oxide and the linkers include silanes as functional groups.

21. A solution or dispersion consisting essentially of metal particles of nanometre dimensions dissolved or dispersed in an electron donor solvent.

22. A solution or dispersion as claimed in claim

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21 in which the metal particles are colloids of from 10-500 nm.

23. A solution or dispersion as claimed in claim 21, in which the metal particles are clusters of from 0.5 to 10 nm.

24. A solution or dispersion as claimed in any of claims 21 to 23, in which the electron donor solvent is selected from the group consisting of benzenoid compounds, and heterocyclic compounds which can donate π electrons.

25. A solution or dispersion as claimed in claim 24, in which the electron donor solvent is an aromatic solvent selected from the group consisting of toluene, benzene, pyridine, anisole, methylnaphthalene, aniline, xylene and mixtures of the above with polycyclic aromatic compounds such as m-terphenyl, naphthalene and phenanthrene.

26. A solution or dispersion as claimed in claim 25 in which the aromatic solvent is toluene.

27. A solution or dispersion as claimed in any of claims 21 to 26 in which hydrophobic quaternary ammonium, phosphonium or arsonium ions are present in the preparation of the solution.

28. A solution or dispersion as claimed in claim 27, in which the hydrophobic quaternary ammonium phosphonium or arsonium ions are C_5 to C_{10} alkyl

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substituted quaternary ammonium, phosphonium or arsonium ions.

29. A solution or dispersion as claimed in claim 28, wherein the quaternary ammonium ions are tetraoctylammonium ions.

30. A solution or dispersion as claimed in any of claims 21 to 29, in which the metal particles are selected from the group consisting of coin metals, transition metals and elements of groups IB to IVB of the periodic table or alloys and which are neither too reactive that the particles coalesce and precipitate out nor so stable that they can't be reacted.

31. A method of producing a solution or dispersion of metal particles of nanometre dimensions, the method comprising

- (1) mixing an aqueous solution or dispersion of a metal salt with an electron donor solvent in the presence of a phase transfer reagent for a period sufficient to allow transfer of the metal as metal ions into the organic phase, and
- (2) conducting a reduction step.

32. A method as claimed in claim 31, wherein the metal salt is a tetrachloroaurate, the organic phase is toluene and the reducing step is conducted using a borohydride.

33. A two step method of producing a bulk

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material which comprises

1) preparing a solution or dispersion of nanometre sized metal or semi-conductor particles which are neither too stable that they cannot be reacted nor so reactive that the particles coalesce and 2) reacting said solution or dispersion of said metal or semi-conductor particles with a solution of polyfunctional linker molecules.

34. A method as claimed in claim 33, wherein the solution is a solution of gold particles in toluene in the presence of tetraoctylammonium ions and said polyfunctional linker molecule is an α, ω alkanedithiol.

35. A method as claimed in claim 33, wherein the solution is a dispersion of TiO_2 particles and said polyfunctional linker molecule is a silane.

36. A one step method of producing a bulk material of particles of nanometre dimensions comprising preparing a solution or dispersion of small metal or semi-conductor particles in the presence of a polyfunctional linker molecule.

37. A method as claimed in claim 36, wherein the solution is a solution of gold particles in diethyl ether in the presence of tetraoctyl ammonium ions and said polyfunctional linker molecule is an α, ω alkanedithiol.

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38. A method as claimed in claim 36, wherein the solution is a dispersion of TiO_2 particles and said polyfunctional linker molecule is a silane.

39. A bulk material comprising particles of nanometre dimensions and linker molecules.

40. A thin film structure comprising a substrate and at least one layer of particles of nanometre dimensions linked thereto by linker molecules.

41. A quantum dot, quantum wire or quantum well device comprising a material as claimed in claim 39 or a thin film structure as claimed in claim 40.

42. A device/material which changes its reflectance with applied potential comprising a thin film structure as claimed in claim 40.

43. A "smart" window comprising a material as claimed in claim 42.

44. A photovoltaic material comprising a material as claimed in claim 40.

45. A PV device comprising a photovoltaic material as claimed in claim 44, comprising nanosized gold particles separated by a 1,1'-di(8 -thiolo-octyl) ferrocene linkers

46. A solid state sensitised PV semiconductor device comprising a photovoltaic material as claimed in claim 44.

47. A solid state sensitised PV semiconductor

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device as claimed in claim 46, comprising nanosized TiO_2 particles.

48. An I.R. reflector comprising an infrared material as claimed in claim 42 in which the particle size is homogeneous.

49. A magnetic device comprising a material as claimed in claims 39 or 40.

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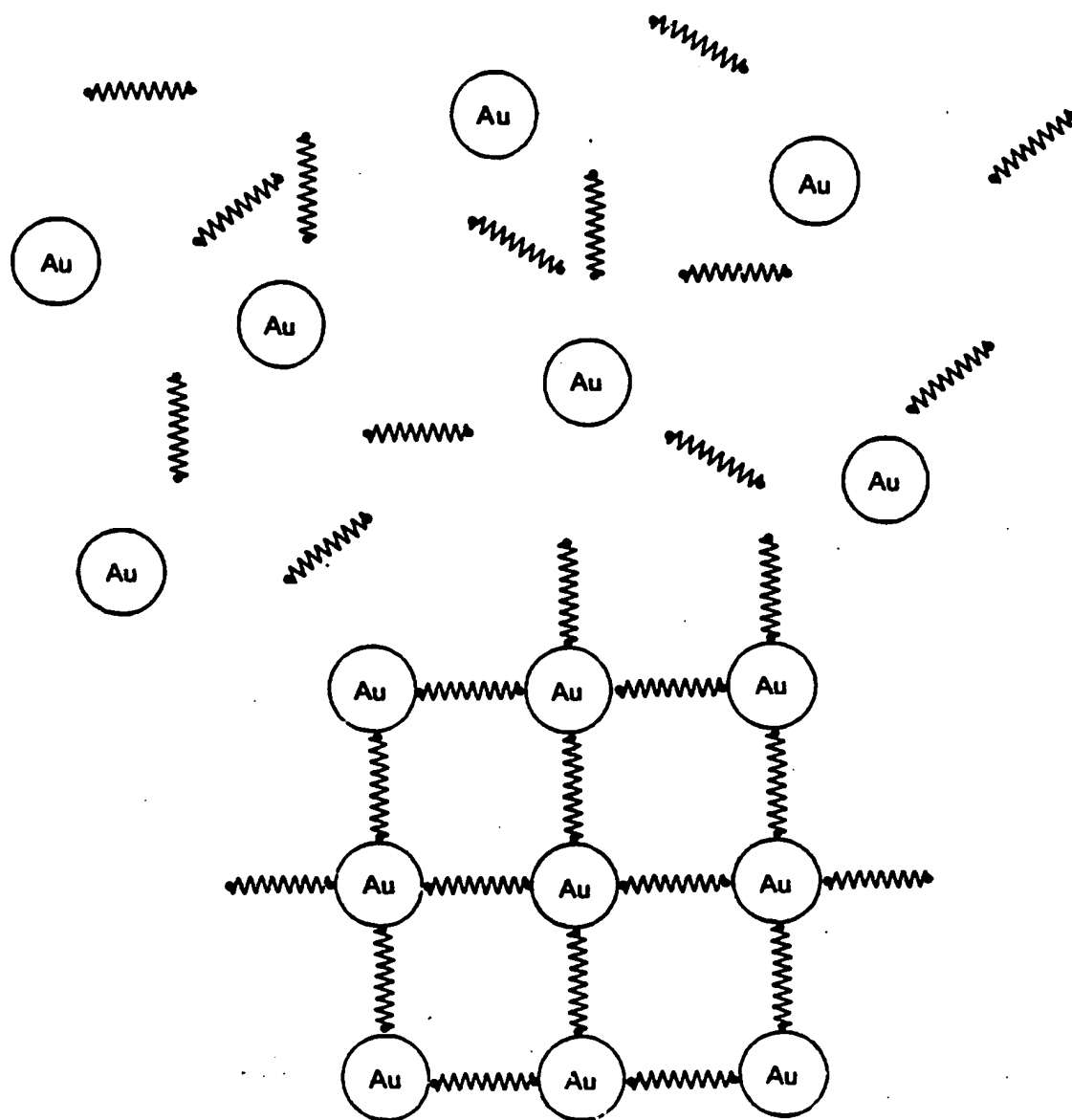


FIG. 1

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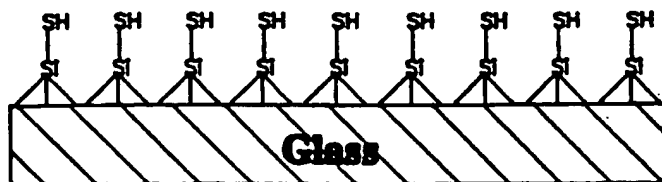
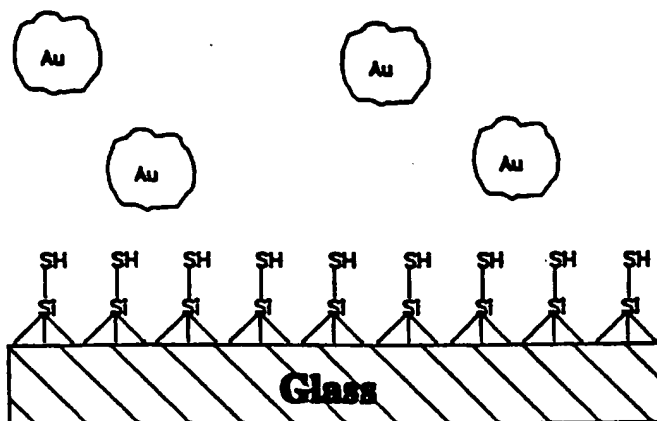
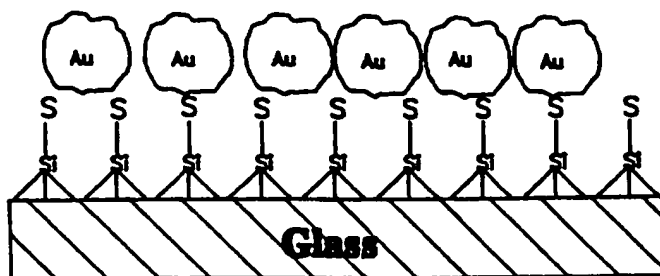
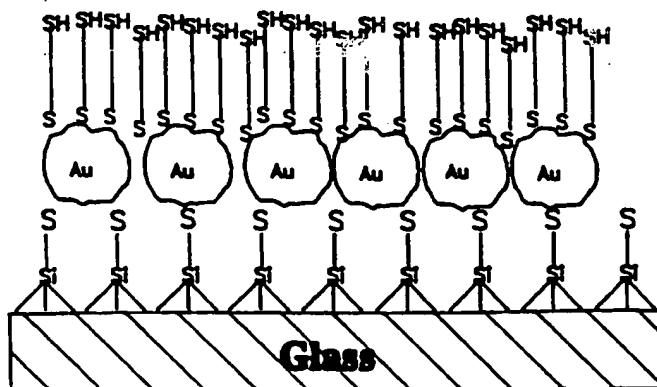
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FIG. 2
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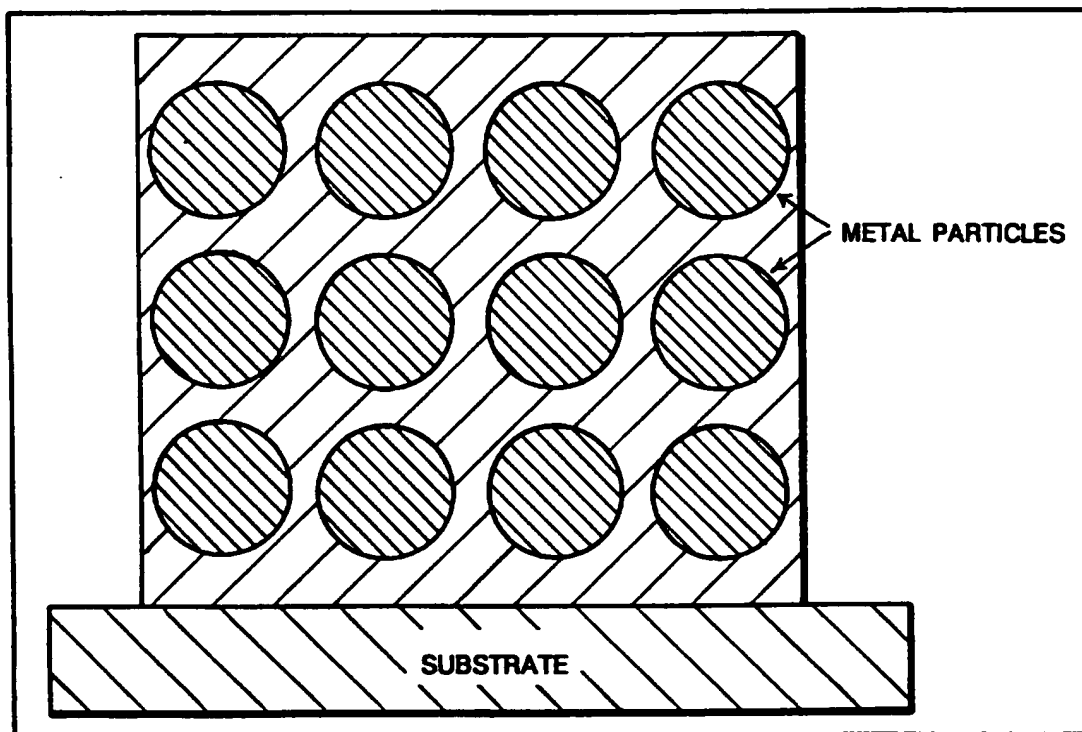


FIG. 3

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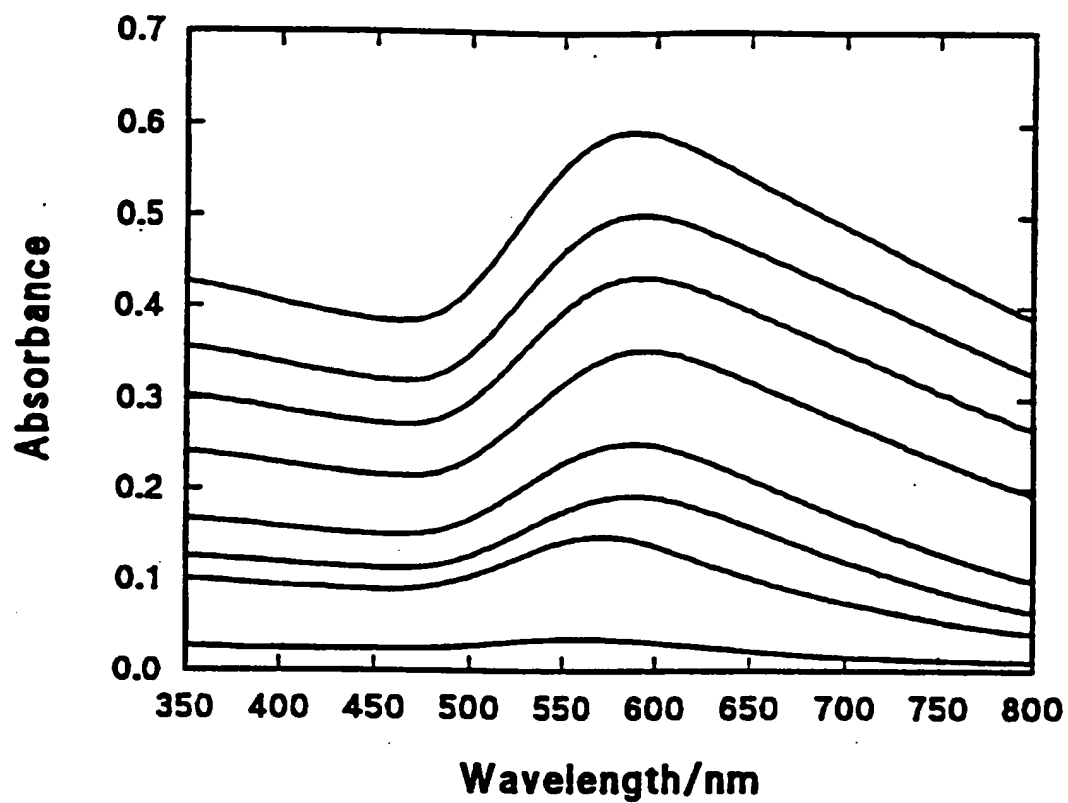


FIG. 4

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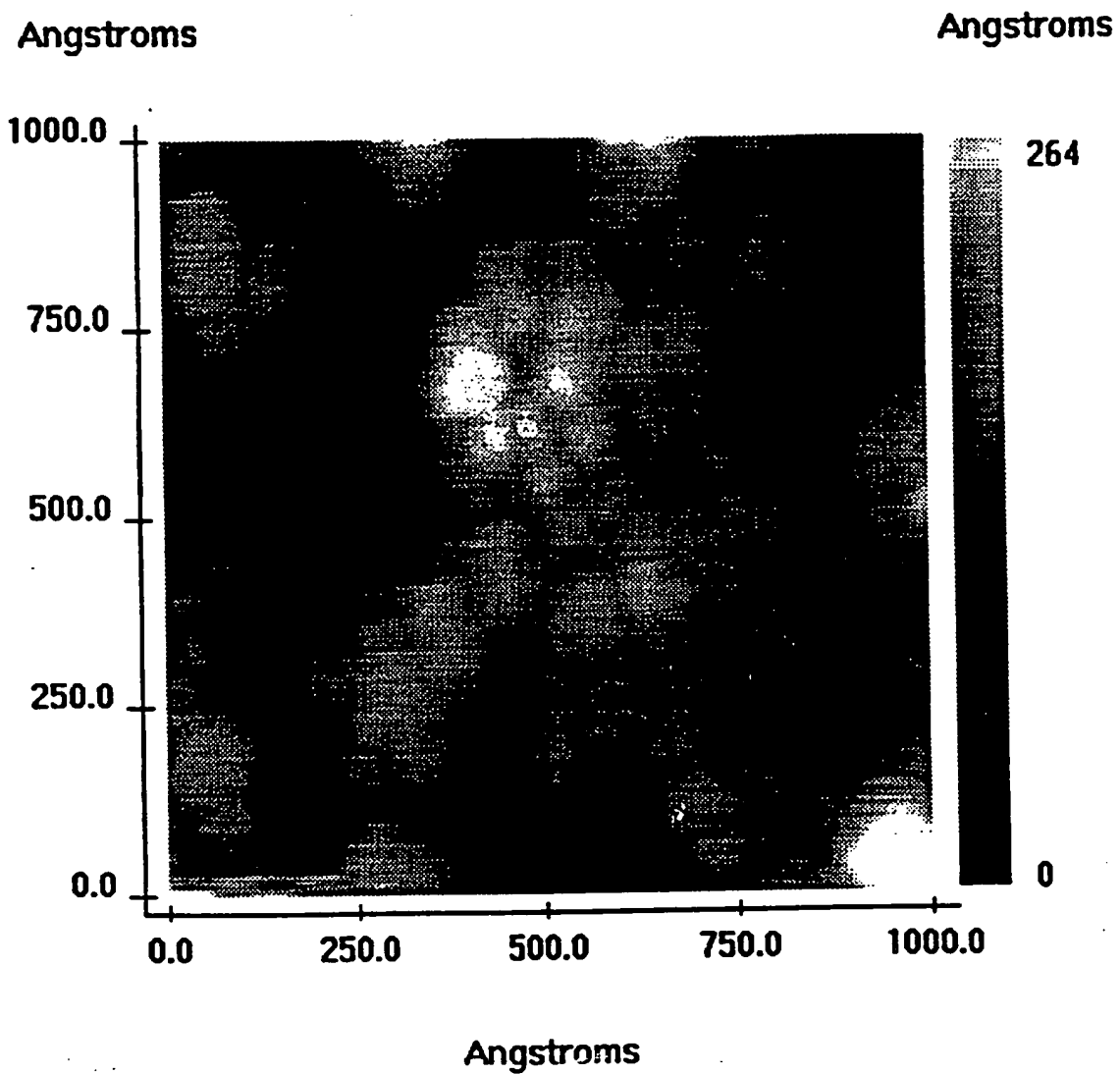


FIG. 5

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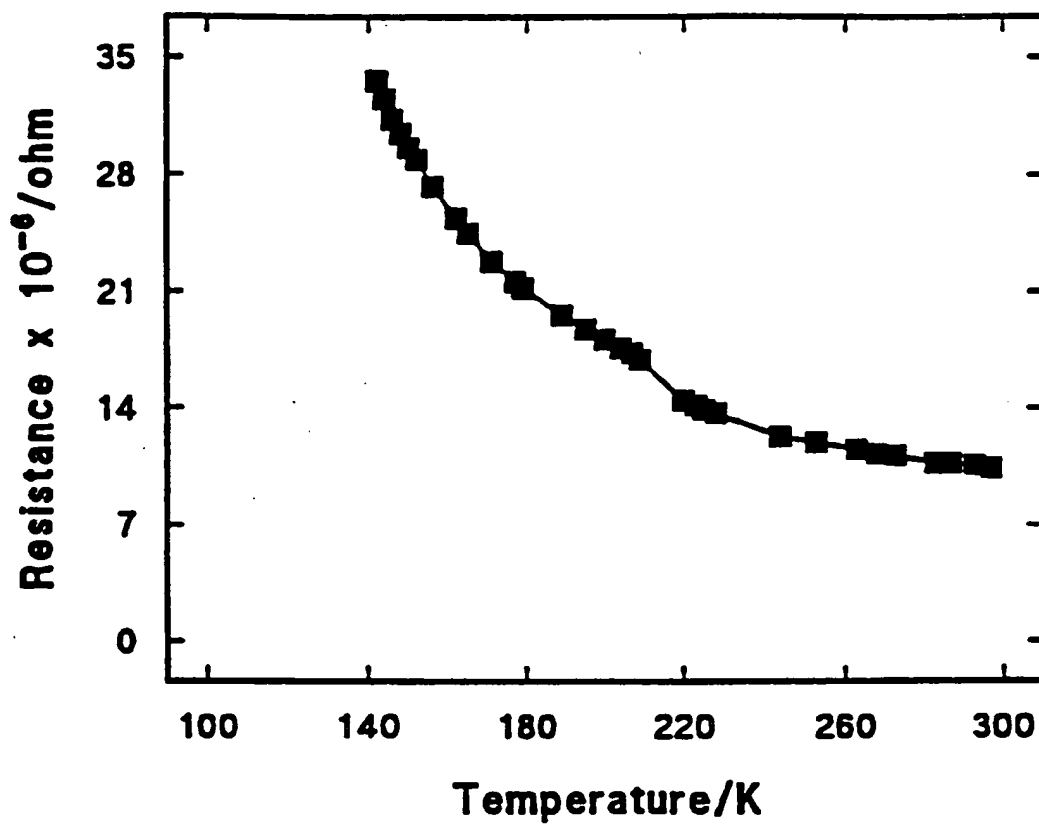


FIG. 6

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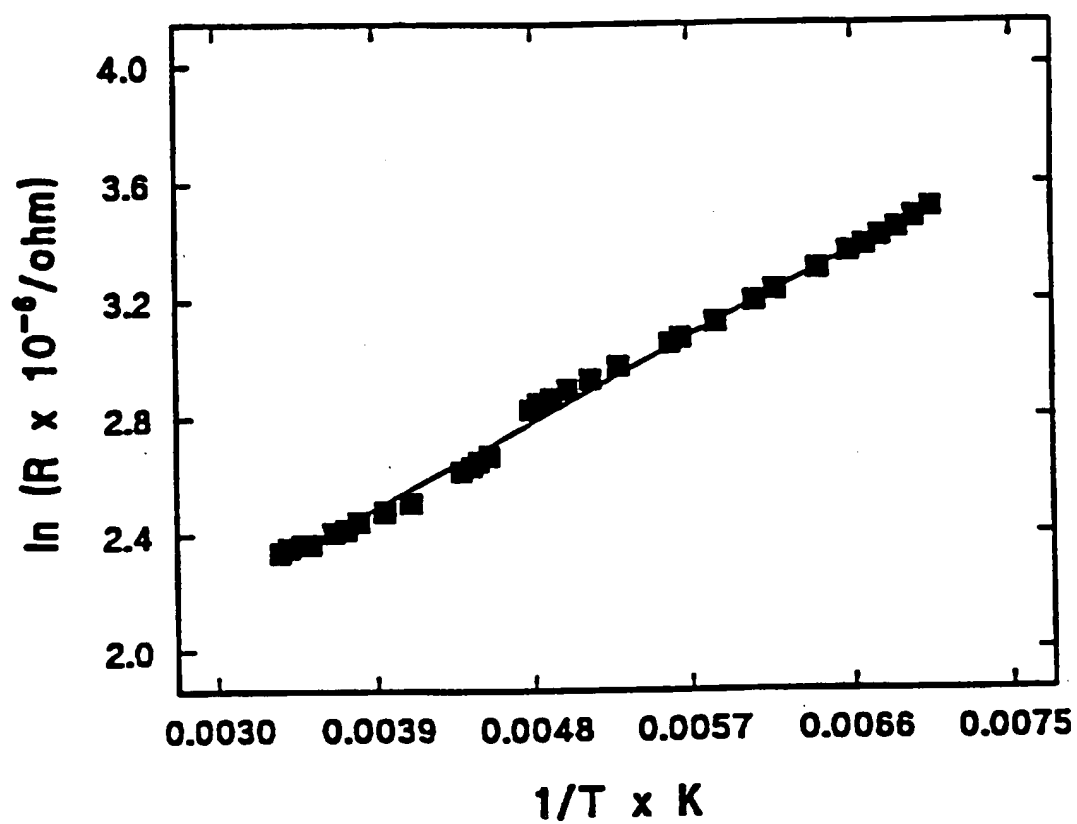


FIG. 7

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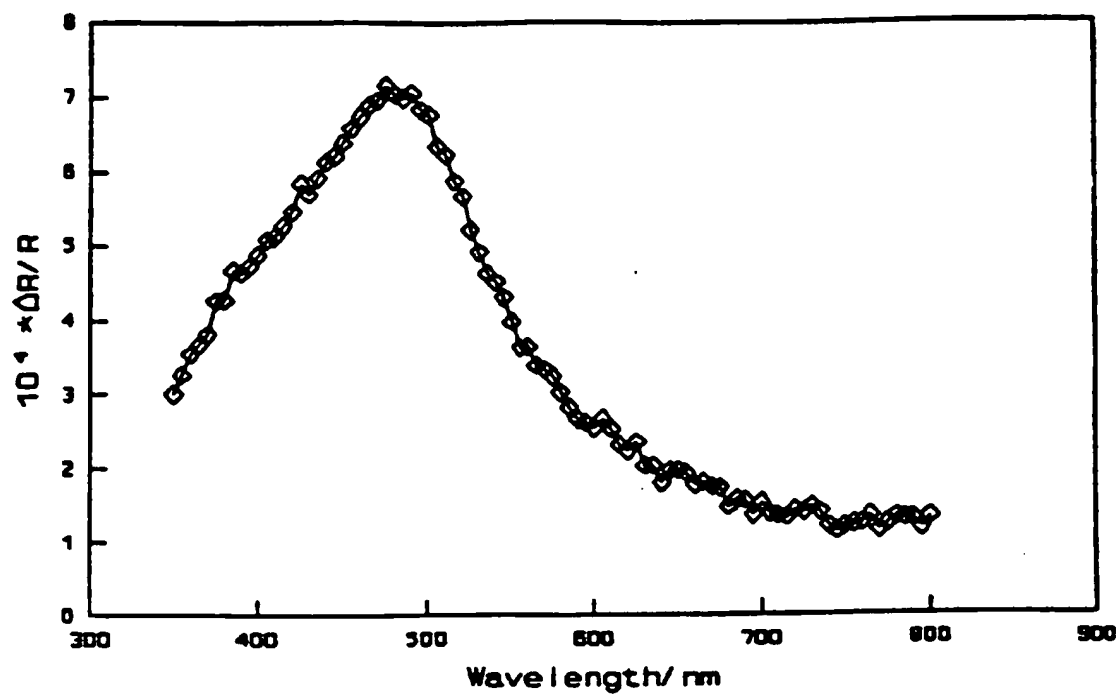


FIG. 8

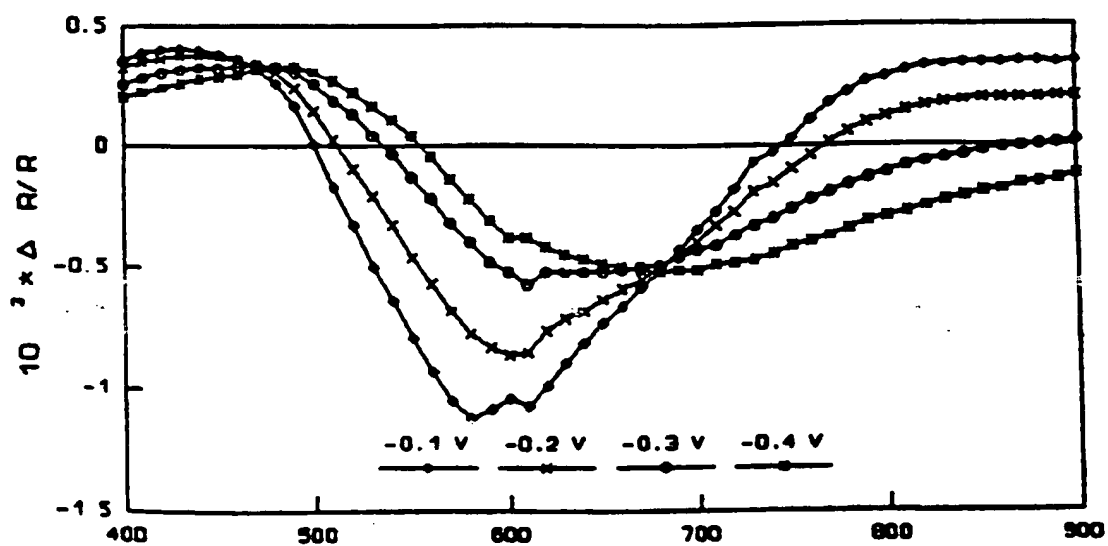


FIG. 9

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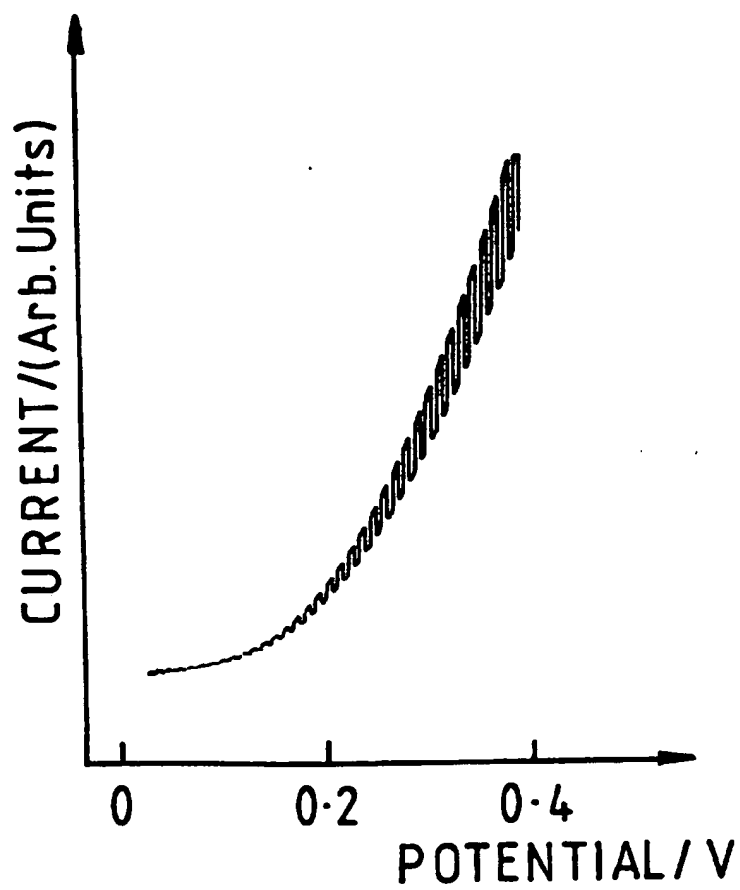


FIG. 10

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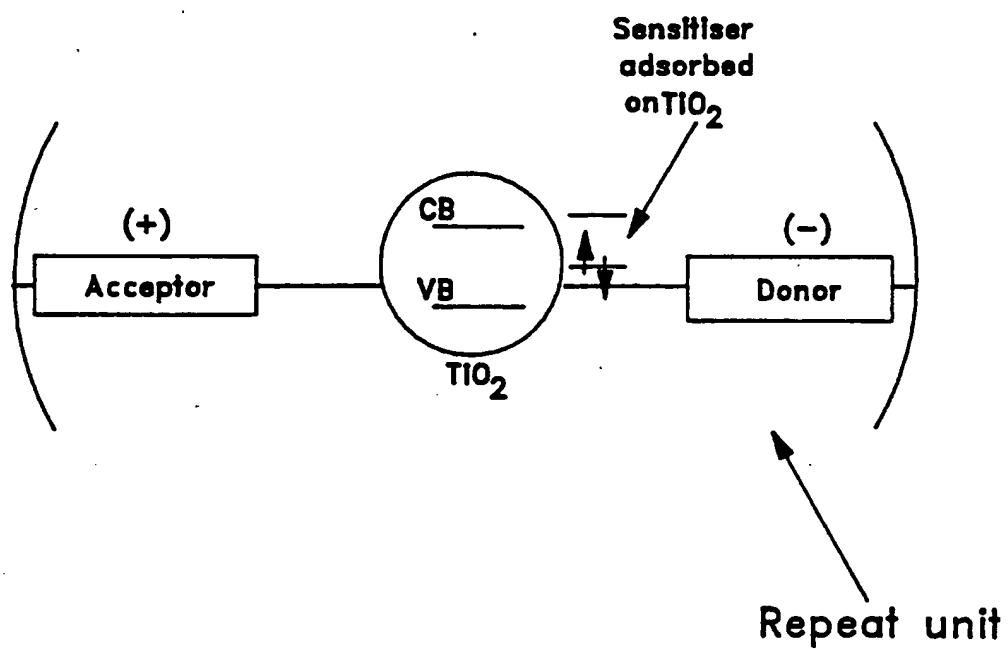


FIG. 11

INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/GB 95/02124

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B05D1/18 B05D7/00 C09K9/02 C03C17/34 H01L29/12
H01L51/20 H01L51/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03C H01L B05D C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	JOURNAL OF COLLOID AND INTERFACE SCIENCE, vol. 110, no. 1, January 1986 pages 82-87, Y. NAKAO ET AL. 'Preparation of noble metal sols in the presence of surfactants and their properties' see the whole document ----- -/--	21-23

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

15 January 1996

Date of mailing of the international search report

22 01 96

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Authorized officer

Brothier, J-A

INTERNATIONAL SEARCH REPORT

Intern. Appl. Application No

PCT/GB 95/02124

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMISTRY IN AUSTRALIA, vol. 59, no. 12, December 1992 pages 617-619, D.N. FURLONG ET AL. 'Surfactant/particle Films for non-linear Optics' see the whole document ---	1,2,4,6, 9-11,14, 17,18, 40,41
P,X	EP,A,0 622 439 (N.V. PHILIPS GLOEILAMPENFABRIEKEN) 2 November 1994 see the whole document ---	39,41
X	WO,A,93 10564 (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA) 27 May 1993 see the whole document ---	1,2, 10-19
X	ADVANCED MATERIALS, vol. 5, no. 1, January 1993 WEINHEIM DE, pages 55-57, XP 000331746 A. ULMAN 'Self-Assembly of Semiconductor Nanocrystals' see the whole document ---	1,2, 10-13, 15-19
X	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 114, 1992 DC US, pages 5221-5230, V.L. COLVIN ET AL. 'Semiconductor nanocrystals covalently bond to metal surfaces with self-assembled monolayers' see the whole document ---	1,2, 10-19
P,X	COLLOID AND POLYMER SCIENCE, vol. 273, no. 2, February 1995 pages 101-117, G. SCHOEN ET AL. 'A fascinating new field in colloid science: small ligand stabilized metal clusters and possible application in microelectronics Part I: State of the art' see page 102, line 9 - page 103, right column ---	39-41
X	YI, KYUNGHEE CHOI 'METALLIC AND SEMICONDUCTOR NANOPARTICULATE FILMS GENERATED UNDER MONOLAYERS AND BETWEEN LANGMUIR-BLODGETT FILMS' 1993, UMI DISSERTATION SERVICES see page 14 - page 17 see page 57 - page 102 see page 217 - page 235 ---	1,6-11, 13-19, 21-23, 27,30,36

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INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/GB 95/02124

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PHYSICAL REVIEW LETTERS, vol. 72, no. 3, 17 January 1994 NEW YORK US, pages 416-419, R.N.BHARGAVA ET AL. 'Optical Properties of Manganese-Doped Nanocrystals of ZnS' see page 416, left column, paragraph 2 -----</p>	21,23-26

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Appl. No.

PCT/GB 95/02124

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-622439	02-11-94	JP-A- 6349579	22-12-94
WO-A-9310564	27-05-93	EP-A- 0613585	07-09-94
		JP-T- 7502479	16-03-95